Professor Rich G. Carter
Oregon State University

Annual Reports

(Due September 15 of every year at 5 pm)

For those of you who are new, what I am looking for is an appropriately written experimental with full characterization of all NEW compounds you have made during the last 12 months. Also, if you have developed a modified procedure for a known compound (including a procedure developed initially by us), please write a proper experimental for that as well. All new compounds must be fully characterized: 1H, 13C, IR, HRMS, [alpha]D (if chiral) and mp (if a solid). COSY's are now required for all new compounds. I have included some sample experimentals to follow. I would ask that you include the ChemDraw header as well. Please note sizing on Chem Draw image in Word (shrink 70% in word). Also, please note subtle line spacing issues in examples!! Keep them consistent!!

Please make sure to include a book and page number reference at the beginning of EACH experimental procedure (no exceptions). The format should be as follows:

[Your Initials]-[Book number as roman numeral]-[page number]

DO NOT GET CREATIVE IN THE EXPERIMENTAL SECTION. FOLLOW EXACTLY THE WRITING STYLE IN THE EXAMPLES. YOU ARE NOT WRITING A PULITZER-AWARD WINING NOVEL HERE!!

I would also ask that you submit schemes (Chem Draw) which outline the reactions you have done (with yields and conditions). You do not have to include every single reaction; however, I would ask that you include routes that failed as well succeeded. These schemes really help when I write the manuscripts and when you write a thesis.

Finally, I will ask that you give me a folder for each new compound. The outside of the folder should have the structure drawn on the tab and the spectra characterizations that you have obtained written on the outside front cover. I also ask that you write the [alpha]D values on the outside of the folder (include the observed rotation with sign, the concentration and the actual [alpha]D). Please note if your [alpha]D is NOT done in CHCl3. Inside the folder should be all of your spectra....including crude NMR's. If you would like, you can include a copy of the experimental procedure within the folder in addition to the copy of the experimentals that you are preparing separately.

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Your 1H should be formatted 10 to -0.5 ppm with integrals and the tallest peak on-scale. Also, zoomed in regions of major grouping of signals are helpful (especially signals that fall outside the official range). Make sure you get a peak printout as well.

Your 13C should be formatted from 220 to -10 ppm with the tallest peak on-scale. For dilute samples, an additional spectra with the CDCl3 (or other solvent) blown off-scale would be appropriate. Also, zoomed in regions of major grouping of signals are helpful (especially signals that fall outside the official range). Make sure you get a peak printout as well.

Please make sure your 1H and 13C are as free from impurities as possible (including solvent!!!) This may sound tedious, but I plan to submit copies of our 1H and 13C NMR for every compound we make with every publication. Place the "for publication 1H and 13C spectra" at the front of the folder.

I want our published experimentals to develop the reputation for being highly reliable. That goal all starts with you. The experimentals that you give to me will to be used in our papers. For the grad students, this will also be a HUGE timesaver when it comes to writing your thesis.

If you got any questions, please ask.

Professor Rich G. Carter
Oregon State University

Enantioselective Total Synthesis of Lycopodine

Hua Yang, Rich G. Carter* and Lev N. Zakharov

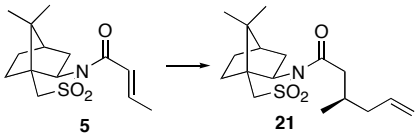
Department of Chemistry, Oregon State University, Corvallis, OR 97331

Electronic Supplementary Information: Experimental

General. Infrared spectra were recorded neat unless otherwise indicated and are reported in cm^{-1}. ^{1}H NMR spectra were recorded in deuterated solvents and are reported in ppm relative to tetramethylsilane and referenced internally to the residually protonated solvent. ^{13}C NMR spectra were recorded in deuterated solvents and are reported in ppm relative to tetramethylsilane and referenced internally to the residually protonated solvent.

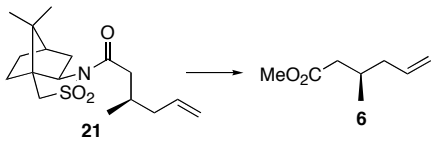
Routine monitoring of reactions was performed using EM Science DC-Alufolien silica gel, aluminum-backed TLC plates. Flash chromatography was performed with the indicated eluents on EM Science Gedurian 230-400 mesh silica gel.

Air and/or moisture sensitive reactions were performed under usual inert atmosphere conditions. Reactions requiring anhydrous conditions were performed under a blanket of argon, in glassware dried in an oven at 120°C or by flame, then cooled under argon. Dry THF and DCM were obtained via a solvent purification system. All other solvents and commercially available reagents were either purified via literature procedures or used without further purification.



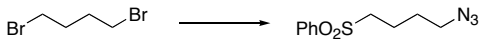
5 21

Sultam 21: $CuBr{\bullet}SMe_2$ (7.83 g, 38.1 mmol) and LiCl (1.77 g, 41.8 mmol) were dissolved in THF (75 mL). The resulting solution was added to allylmagnesium bromide (34.4 mL, 31.3 mmol, 0.91 M in Et_2O) at –78°C *via* syringe. TMSCl (4.89 mL, 39.2 mmol) was then added followed by a solution of 5[11] (7.40 g, 26.1 mmol) in THF (75 mL) after which the clear brown reaction mixture. After for 90 min, the reaction was quenched with aq. NH_4Cl-NH_4OH (9:1, pH 9, 90 mL), warmed to rt and partitioned between Et_2O (50 mL) and water (50 mL). The aqueous layer was extracted with EtOAc (3 X 100 mL). The organic phase was washed with sat. aq. NaCl (100 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* and purified by chromatography over silica gel, eluting with 5-10% EtOAc / Hexanes, to give known 21[2] (7.27 g, 22.4 mmol, 86%) as a white solid: $[\alpha]_D^{23}$ = -88° (*c* = 3.6, $CHCl_3$); IR (neat) 2961, 1680, 1389, 1326, 1272, 1241, 1139, 1061, 918, 778, 615 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.70-5.83 (m, 1H), 5.00-5.05 (m, 2H), 3.88 (t, *J* = 6.3 Hz, 2H), 3.46 (q, *J* = 14.0 Hz, 2H), 2.76 (dd, *J* = 16.0, 6.3 Hz, 1H), 2.49 (dd, *J* = 16.0, 7.5 Hz, 1H), 1.87-2.29 (m, 8H), 1.32-1.45 (m, 2H), 1.16 (s, 3H), 0.98 (s, 3H), 0.97 (d, *J* = 6.8 Hz, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 136.5, 116.6, 65.2, 53.0, 48.3, 47.7, 44.7, 42.1, 40.9, 38.6, 32.8, 29.7, 26.5, 20.8, 19.9, 19.6; HRMS (EI+) calcd. for $C_{17}H_{27}NO_3S$ (M+) 325.1722, found 325.



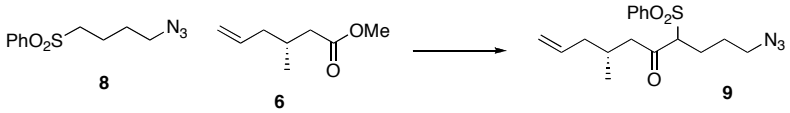
21 **6**

Methyl Ester 6: To a solution of **21** (6.92 g, 21.4 mmol) in CH_2Cl_2 / MeOH (1:1, 105 mL) was added $Mg(OMe)_2$ (36.8 mL, 53.4 mmol, 1.45 M in MeOH) at 0ºC. After 3 h, the reaction mixture was quenched with sat. aq. NH_4Cl (40 mL) and extracted with CH_2Cl_2 (3 X 50 mL). The dried (Na_2SO_4) extract was concentrated *in vacuo*. The resulting mixture was extracted with hexanes (2 X 20 mL) and concentrated *in vacuo* to give known **6**[2] (3.00 g, 21.1 mmol, 99%) as a colorless liquid: $[\alpha]_D^{23}$ = +3° (*c* = 3.47, $CHCl_3$); IR (neat) 2954, 2922, 1734, 1434, 1261, 1222, 1173, 1005, 917cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.69-5.82 (m, 1H), 5.02 (d, *J* = 13.0 Hz, 2H), 3.66 (s, 3H), 2.26-2.36 (m, 1H), 1.98-2.14 (m, 4H), 0.95 (d, *J* = 5.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 136.4, 116.6, 51.3, 41.0, 40.8, 30.1, 19.6; HRMS (EI+) calcd. for $C_8H_{14}O_2$ (M+) 142.0994, found 142.1217.



7 **8**

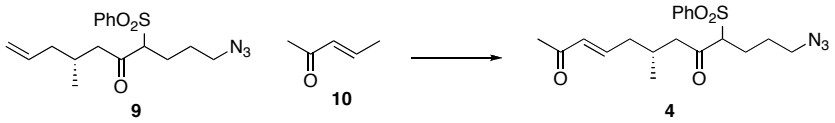
Sulfone 8: To a solution of 1,4-dibromobutane (**7**) (21.7 g, 12.0 mL, 100.5 mmol) in DMF (400 mL) was added $NaSO_2Ph$ (16.5 g, 100.5 mmol) over a 30 min period. After stirring for 5 h, NaN_3 (7.84 g, 120.6 mmol) and water (40 mL) were added to the reaction mixture. The mixture was warmed to 50ºC. After 6 h, the reaction mixture was poured into ice water (240 mL). The resulting solution was extracted with diethyl ether (3 X 200 mL). The dried (Na_2SO_4) extract was concentrated *in vacuo* and purified by chromatography over silica gel, eluting with 50-70% diethyl ether / hexanes, to give **8** (11.2 g, 46.9 mmol, 47%) as a colorless oil: IR (neat) 2942, 2090, 1445, 1299, 1140, 1088 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92-7.94 (m, 2H), 7.58-7.72(m, 3H), 3.31 (t, *J* = 6.6 Hz, 2H), 3.14 (t, *J* = 7.5 Hz, 2H), 1.64-1.89 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.0, 133.8, 129.4, 128.1, 55.7, 5.07, 27.6, 20.2; HRMS (CI+) calcd. for $C_{10}H_{14}N_3O_2S$ (M+H) 240.0806, found 240.0807.



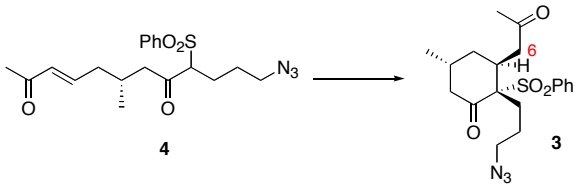
8 **6** **9**

Keto sulfone 9: To a stirred solution of **8** (2.52 g, 10.55 mmol) in THF (120 mL) at –78°C was added lithium 2,2,6,6-tetramethylpiperidine[3] (21.1 mL, 21.1 mmol, 1.0 M in THF) dropwise. After 5 min, a solution of **6** (3.00 g, 21.1 mmol) in pre-cooled THF (5 mL) was added via cannula to the sulfone solution. After stirring at -78 to -20 ºC for 90 min, the reaction was removed from the cooling bath, quenched with sat. aq. NH_4Cl (40 mL) and extracted with Et_2O (3 X 50 mL). The dried (Na_2SO_4) extract was concentrated *in vacuo* and purified chromatography over silica gel, eluting with 5-20% EtOAc / hexanes, to give **9** (2.72 g, 7.79 mmol, 74%) as a colorless oil: IR: (neat) 2959, 2929, 2873, 2095,

1712, 1449, 1320, 1153, 1084, 912, 748, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, two diastereomers) δ 7.80-7.82 (m, 2H), 7.71-7.75 (m, 1H), 7.59-7.61 (m, 2H), 5.73-5.79 (m, 1H), 5.03-5.08 (m, 2H), 4.11-4.16 (m, 1H), 3.26-3.30 (m, 2H), 2.93 (dd, *J* = 18.4, 5.2 Hz, 1H), 2.62-2.80 (m, 1H), 2.48 (dd, *J* = 18.4, 7.2 Hz, 1H), 1.87-2.15 (m, 5H), 1.46-1.80 (m, 2H), 0.97 (d, *J* = 6.4 Hz, 3H), 0.94 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.6, 201.4, 136.34, 136.25, 136.20, 136.1, 134.5, 129.45, 129.43, 129.2, 116.9, 74.7, 74.4, 51.8, 51.6, 50.8, 40.9, 40.6, 28.3, 28.0, 26.3, 24.7, 24.6, 19.60, 19.57; HRMS (ES+) calcd. for $C_{17}H_{23}N_3O_3NaS$ (M+Na) 372.1358, found 372.1333.

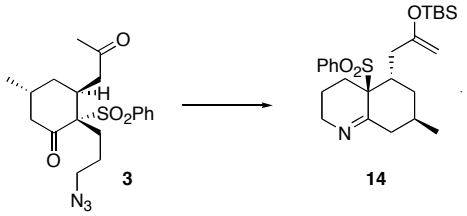


Enone 4: A solution of degassed 2nd Gen. Hoveyda-Grubbs catalyst (1.34 mg, 21.5 *μ*mol) in CH_2Cl_2 (0.22 mL) and 3-penten-2-one[4] (**10**) (54mg, 90 μL, 0.645 mmol, 70% pure) was added to alkene **9** (150 mg, 0.430 mmol). After 2 h, the reaction was cooled at 0 ºC for 10 min and loaded directly onto silica gel. It was purified by chromatography, eluting with 10-30% EtOAc / hexanes, to give **4** (106 mg, 0.270 mmol, 63%) as colorless oil as well as recovered **9** (43 mg, 0.122 mmol, 28%): IR (neat) 2927, 2959, 2094, 1718, 1664, 1631, 1451, 1364, 1310, 1152, 743. 689, 591 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, two diastereomers) δ 7.80 (d, *J* = 7.6 Hz, 2H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 2H), 6.71-6.80 (m, 1H), 6.08- 6.14 (m, 1H), 4.12-4.15 (m, 1H), 3.22-3.31 (m, 2H), 2.87-3.01 (m, 1H), 2.55-2.63 (m, 2H), 2.28 (s, 3H), 2.27 (s, 3H), 2.07-2.34 (m, 2H), 1.91-1.96 (m, 2H), 1.47-1.50 (m, 2H), 1.00 (d, *J* = 6.4 Hz, 3H), 0.97 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 200.9, 198.5, 198.4, 145.6, 136.13, 136.08, 134.6, 133.1, 133.0, 129.4, 129.2, 74.6, 74.5, 51.8, 51.6, 50.8, 39.3, 38.9, 27.91, 27.85, 27.1, 26.3, 24.72, 24.65, 19.73, 19.65; HRMS (ES+) calcd. for $C_{19}H_{25}N_3O_4NaS$ (M+Na) 414.1463, found 414.1459.

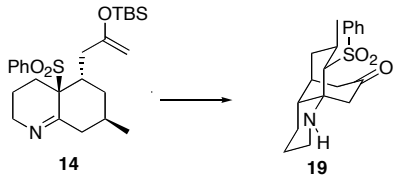


Cyclohexanone 3: To a solution of keto sulfone **4** (0.415 g, 1.06 mmol) in CH_2Cl_2 / Isopropanol (1:4, 5 mL) was added diisopropylamine (0.644 g, 0.89 mL, 6.37 mmol) at room temperature. After 13 h, the solvent was removed *in vacuo.* The reaction mixture was loaded directly onto silica gel and was purified by chromatography, eluting with 10-30% EtOAc / hexanes, to give the product **3** (0.369 g, 0.944 mmol, 89%) as a white solid. Mp 108-109 ºC (recrystallized from hexanes); $[\alpha]_D^{23}$ = +145° (*c* = 1.04, $CHCl_3$); IR (neat) 2960, 2927, 2873, 2105, 1718, 1451, 1364, 1299, 1141, 754, 721, 694, 618 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.2 Hz, 2H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 2H), 3.66-3.70 (m, 1H), 3.22-3.28 (m, 2H), 3.09 (d, *J* = 16.8 Hz, 1H), 2.77 (dd, *J* =

14.4, 9.6 Hz, 1H), 2.48-2.56 (m, 2H), 2.24 (s, 3H), 1.55-2.07 (m, 7H), 1.05 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.84, 205.77, 135.8, 134.3, 130.1, 128.9, 77.9, 51.5, 47.0, 44.1, 34.0, 31.8, 30.4, 27.5, 26.9, 23.9, 21.5; HRMS (ES+) calcd. for $C_{19}H_{25}N_3O_4NaS$ (M+Na) 414.1463, found 414.1468.

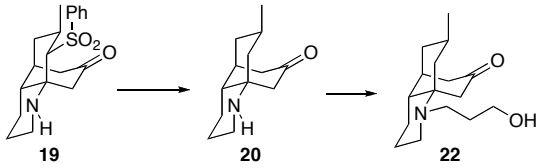


Imine 14: To a solution of **3** (400 mg, 1.02 mmol) in THF (31 mL) was added PPh_3 (0.262 g, 1.02 mmol). The reaction mixture was heated to reflux. After 5 h, the reaction was cooled to rt and the solvent was removed *in vacuo* to give crude imine. This crude imine was immediately redissolved in CH_2Cl_2 (10 mL), cooled to 0°C and *i*-Pr_2NEt (0.824 g, 1.1 mL, 6.38 mmol) was added to the solution. After 1 min, TBSOTf (0.674 g, 0.59 mL, 2.55 mmol) was added dropwise. After 5 h, the reaction was removed from the cooling bath, quenched with sat. aq. $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (3 X 15 mL). The dried (K_2CO_3) extract was concentrated *in vacuo* purified by chromatography over alumina, eluting with 2-10% EtOAc / hexanes, to give **14** (362 mg, 0.834 mmol, 82%) as a colorless oil: $[\alpha]_D^{23}$ = +81° (*c* = 1.6, $CHCl_3$); IR (neat) 2954, 2927, 2856, 1631, 1468, 1446, 1310, 1141, 1010, 841, 776, 694, 607 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83-7.85 (m, 2H), 7.63-7.68 (m, 1H), 7.52-7.57 (m 2H), 4.10 (s, 1H), 4.03 (s, 1H), 3.65 (d, *J* = 15.6 Hz, 1H), 3.07 (td, *J* = 12.6, 3.9 Hz, 1H), 2.85-2.89 (m, 1H), 2.41-2.50 (m, 3H), 2.11-2.14 (m, 2H), 1.56-2.02 (m, 6H), 1.05 (d, *J* = 6.6 Hz, 3H), 0.93 (s, 9H), 0.20 (s, 3H), 0.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 156.1, 137.0, 133.7, 130.0, 129.0, 128.7, 92.0, 69.4, 48.0, 45.7, 38.6, 37.1, 31.7, 29.7, 28.6, 27.7, 25.7, 22.1, 20.7, 18.0, -4.78, -4.83; HRMS (CI+) calcd. for $C_{25}H_{40}NO_3SiS$ (M+1) 462.2498, found 462.2480.

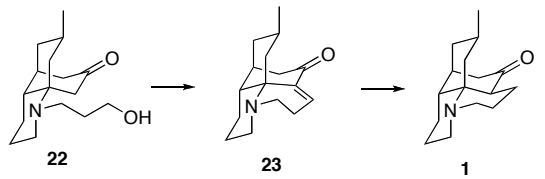


Tricycle 19: To a solution of **14** (256 mg, 0.589 mmol) in dry 1,2-dichloroethane (23 mL) was added $Zn(OTf)_2$ (0.643 g, 1.77 mmol). The reaction mixture was heated at 96 ºC in a sealed tube. After 16 h, the reaction was cooled to rt, quenched with sat. aq. $NaHCO_3$ (5 mL) and extracted with CH_2Cl_2 (3 X 10 mL). The dried (K_2CO_3) extract was concentrated *in vacuo* and purified chromatography over silica gel, eluting with 1-10% MeOH / CH_2Cl_2, to give **19** (104 mg, 0.300 mmol, 54%) as a white solid. Mp 207-208 ºC (recrystallized from CH_2Cl_2 / hexanes); $[\alpha]_D^{23}$ = +9° (*c* = 0.4, $CHCl_3$); IR (neat) 3357, 2927, 2856, 1702, 1473, 1304, 1288, 1135, 1081, 912, 765, 721, 694 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.55-7.65 (m, 3H), 4.14 (s br, 1H), 3.33

(d, *J* = 11.2 Hz, 1H), 3.20 (d, *J* = 17.2 Hz, 1H), 3.07 (d, *J* = 17.2 Hz, 1H), 2.90-3.00 (m, 2H), 2.54 (dd, *J* = 16.8, 6.4 Hz, 1H), 2.21-2.30 (m, 2H), 2.03 (s br, 1H), 1.63-1.81 (m, 5H), 1.48 (td, *J* = 13.2, 3.6 Hz, 1H), 0.78 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.8, 143.9, 133.1, 129.1, 127.2, 81.7, 59.8, 44.3, 43.0, 41.4, 41.2, 40.6, 34.5, 28.5, 26.1, 25.4, 22.3; HRMS (EI+) calcd. for $C_{19}H_{25}NO_3S$ (M+) 347.1555, found 347.1560.



Alcohol 22: To a stirred solution of **19** (89 mg, 0.256 mmol) in THF (2.5 mL) and MeOH (7.5 mL) at –10°C was added Na_2HPO_4 (254 mg, 1.792 mmol). After 1 min, 5% Na / Hg amalgam (708 mg, 1.539 mmol, 5% in Hg) was added. After 1 h, the reaction was diluted with 20% EtOAc / hexanes, filtered through a small plug of alumina, concentrated *in vacuo* to give crude amine. The crude amine **20** (0.256 mmol) in acetone (2.6 mL) was added K_2CO_3 (75 mg, 0.543 mmol) and $NaHCO_3$ (75 mg, 0.892 mmol) followed by 3-iodo-1-propanol (71 mg, 37 μL, 0.384 mmol). The reaction mixture was heated to reflux. After 6 h, the reaction was cooled to rt and the solvent was removed *in vacuo.* The reaction mixture was purified by chromatography over silica gel, eluting with 1-10% MeOH / CH_2Cl_2, to give known **22**[5] (46 mg, 0.174 mmol, 68%) as a light yellow liquid. $[\alpha]_D^{23}$ = -11° (*c* = 0.9, $CHCl_3$); IR (neat) 3320, 2900, 1700, 1460, 1410, 1335, 1310, 1220, 1170, 1110, 1060, 980, 725 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76-3.86 (m, 2H), 3.07-3.15 (m, 2H), 2.68 (d, *J* = 17.0 Hz, 1H), 2.51 (dd, *J* = 17.0, 7.0 Hz, 1H), 2.3-1.3 (m, 16H), 1.19 (t, *J* = 11.0 Hz, 1H), 0.93 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.3, 64.4, 59.3, 48.4, 46.8, 46.6, 44.0, 42.4, 41.7, 39.1, 35.9, 27.8, 25.81, 25.75, 25.5, 22.6; HRMS (EI+) calcd. for $C_{16}H_{27}NO_2$ (M+) 265.2027, found 265.2042.



Lycopodine (1): To a mixture of *t*BuOK (20.1 mg, 0.179 mmol) and benzophenone (97.7 mg, 0.536 mmol) in dry benzene (0.1 mL) was added a solution of **22** (7.9 mg, 0.0298 mmol) in dry benzene (0.2 mL). The resulting reaction mixture was heated at 110 ºC in sealed tube. After 50 min, the reaction was cooled to rt, diluted with aq. HCl (0.5 mL, 3 N) and washed with Et_2O (2 X 5 mL). The aqueous phase was neutralized to pH 11 by aq. NaOH (6 N) and extracted with CH_2Cl_2 (3 X 5 mL). The dried (K_2CO_3) extract was concentrated *in vacuo* and used next step immediately. To a stirred solution of crude enone **23** (0.179 mmol) in PhMe (0.3 mL) at room temperature was added $[(PPh_3)CuH]_6$

(29.3 mg, 0.015 mmol). After 2 h, another portion of $[(PPh_3)CuH]_6$ (29.3 mg, 0.015 mmol) was added. After an additional 2 h, the reaction mixture was loaded directly onto alumina, eluting with 10-50% ether / benzene, to give lycopodine (**1**)[6] (4.2 mg, 0.017 mmol, 57%) as a white solid. Mp 126-127°C (recrystallized from Et_2O / hexanes), $[\alpha]_D^{23}$ = -23.2° (*c* = 0.22, EtOH) {lit.[7] $[\alpha]_D^{23}$ = -24.5° (*c* =1.10, 100% EtOH)}; IR (neat) 2922, 2850, 1702, 1451, 1380, 1314, 1255, 1215, 1119, 1092, 1015, 906, 808 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.39 (td, *J* = 14.0, 3.6 Hz, 1H), 3.17 (td, *J* = 12.0, 3.0 Hz, 1H), 2.89 (dd, *J* = 12.0, 2.4 Hz, 1H), 2.66 (dd, *J* = 12.0, 2.4 Hz, 2H), 2.55 (td, *J* = 16.0, 6.4 Hz, 2H), 2.22 (d, *J* = 17.6 Hz, 1H), 2.06-2.11 (m, 3H), 1.20-1.92 (m, 11H), 0.88 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.7, 59.9, 47.2, 46.6, 44.9, 43.1, 42.99, 42.84, 42.4, 36.7, 26.1, 25.3, 25.1, 22.9, 19.5, 18.8; HRMS (EI+) calcd. for $C_{16}H_{25}NO$ (M+) 247.1936, found 247.1948.

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3. **Preparation of LiTMP:** To a solution of 2,2,6,6-tetramethylpiperidine (282.8 mg, 340 μL, 2.0 mmol) in THF (0.86 mL) was added n-BuLi (0.8 mL, 2.0 mmol, 2.5 M in hexanes). The reaction was warmed to -10°C and stirred for 30 min prior to use.

4. We purchase 10 (70% pure) from Aldrich's Flavors and Fragrances division (Aldrich Catalog # W341703, 25 g - $92). The impurity (mesityl oxide) does not affect the performance of the cross metathesis. Alternate sources of 10 were significantly higher in cost and less pure.

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